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CHEMICAL REACTIONS IN SHOCK WAVES.(U)  
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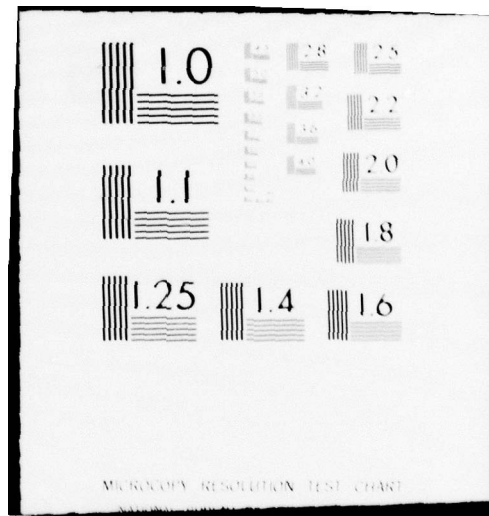
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CHEMICAL REACTIONS IN SHOCK WAVES

FINAL REPORT

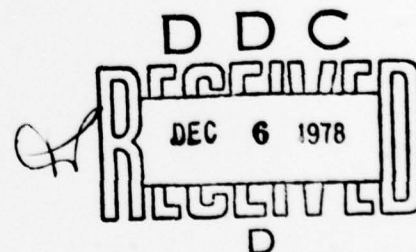
W. C. GARDINER, JR.

OCTOBER 10, 1978

U. S. ARMY RESEARCH OFFICE

GRANT DAHCO4 75 G 0061

THE UNIVERSITY OF TEXAS



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19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Shock waves; high temperatures; chemical kinetics; combustion; explosions; free radicals; detonation.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Experimental and computer modeling studies were carried out on chemical reactions at high temperatures, in particular on reactions which participate in combustion processes. Reaction initiation was by shock-wave heating, and reaction progress was monitored by spectroscopic methods. Systems studied include $CS_2-O_2$ , $CH_4-O_2$ , $CH_4-Ar$ , $C_2H_2-Ar$ , $C_2H_4-Ar$ , and $C_2H_6-Ar$ .		

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## Final Report on Experimental and Modeling Studies of

### Chemical Reactions in Shock Waves

Statement of problems studied. The initial goals of this research were threefold. The first was a technical one, to explore further the use of IR laser absorption spectroscopy for the study of hydrocarbon chemistry at high temperatures. The second was to utilize this technique (together with others) to carry out experiments on important small hydrocarbon pyrolysis and oxidation mechanisms. The third was to undertake an emission spectroscopic investigation of the  $\text{CS}_2\text{-O}_2$  reaction with a view towards better understanding of the mechanism of population inversion of CO produced in the  $\text{CS}_2$  flame laser. Significant results were obtained in all three directions.

Results obtained and discussion. At the time the proposal for this grant was written, we were still engaged in theoretical research on the  $\text{CH}_4$  IR laser absorption and doing experiments on the absorptions of other hydrocarbons. The theoretical work finally led to a coherent description of the  $\text{CH}_4$  absorption as function of temperature, although the critical distinction we had hoped to be able to make with regard to line-broadening models did not materialize. As to the other hydrocarbons, as our data collection continued, our enthusiasm for getting into Zeeman tuning of the Ne or Xe laser lines diminished as our interest in utilizing the totally unexpected high absorptivities for kinetics experiments grew. The  $\text{CH}_4$  results were published in JQSRT, the results for  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$  and  $\text{C}_5\text{H}_{12}$  in Applied Spectroscopy.

The essence of the implication of these results for combustion experiments is that while the lack of specificity was a disappointment, the high absorptivity for the untuned Ne line opened the door for a number of highly successful experiments. Since the writing of this proposal the advent of commercially available tunable diode lasers has rendered Zeeman-tuned rare gas lasers obsolete anyway. Therefore, to pursue the originally contemplated experiments on  $\text{CH}_2\text{O}$  and  $\text{CH}_3$  with IR laser spectroscopy would now entail adding a diode laser to our shock tube. Before undertaking such experiments, however, there are many easier ones begging to be done on the same systems.

Pyrolysis experiments have been done and published on  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$ . The principal techniques were laser-schlieren observations on density gradients and laser-absorption measurements on hydrocarbon disappearance. Data interpretation was done by computer modeling. While the main result in each case was the rate constant for the primary decomposition step, conclusions could also be drawn about the rate constants for important secondary reactions.

Combustion studies were also brought to the publication stage on  $\text{CH}_4$ . In the course of the data interpretation it was found that the relative lack of reactivity of  $\text{CH}_3$  radicals forces a major part of the reaction to proceed via  $\text{C}_2$ -hydrocarbon steps, particularly for rich mixtures. In order to pursue this further, a broad-scale computer modeling effort was made to determine how well a conventional methane combustion mechanism will reproduce  $\text{C}_2$ -hydrocarbon ignition data. The results indicated, primarily, that additional data is needed.

Pyrolysis experiments were also done, but not yet brought into publication form, on the pyrolysis reactions of  $\text{CH}_3\text{I}$ ,  $\text{C}_3\text{H}_8$  and  $\text{C}_4\text{H}_{10}$ . Combustion experiments upon which data analysis is still in progress are on  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$ .

The final major effort on this grant concerned the oxidation of  $\text{CS}_2$ . This reaction was successfully studied using  $\text{SO}_2^+$  luminescence and unsuccessfully studied using IR thermal emission. Computer modeling of the  $\text{SO}_2^+$  results showed a good capability of the mechanism to account for ignition delays, but many basic questions about it remained unanswered. The essential problem with the IR emission experiments, which should have provided a means of probing major product species concentrations during the ignition period, was  $\text{CS}_2$  thermal emission. The broadening of the  $\text{CS}_2$   $\nu_3$  emission band at combustion temperature proved to be so great that it obscured all other emissions in the wavelength region available to us until the end of the ignition delay period. While IR ignition delay measurements were possible, the  $\text{CS}_2$  emission totally prevented attainment of the main object, exponential growth constant measurements. It will be necessary to repeat this study using a broadband IR detector.

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## Bibliography

The following publications resulted from research carried out under this grant:

- J. E. Hardy and W. C. Gardiner, Jr., "Shock Tube Study of Carbon Disulfide Oxidation," Proceedings of the Sixteenth International Symposium on Combustion, MIT, 1976, the Combustion Institute, 1977, p. 985.
- W. C. Gardiner, Jr., "Temperature Dependence of Bimolecular Gas Reaction Rates", Accounts of Chemical Research 10, 326 (1977).
- W. C. Gardiner, Jr., "The pC, pR, pP, pM and pS Method of Formulating the Results of Computer Modeling Studies of Chemical Reactions," Journal of Physical Chemistry 81, 2367 (1977).
- D. B. Olson and W. C. Gardiner, Jr., "An Evaluation of Methane Combustion Mechanisms", Journal of Physical Chemistry 81, 2514 (1977).
- J. E. Hardy, W. C. Gardiner, Jr., and A. Burcat, "Recombination of Carbon Monoxide and Oxygen Atoms", International Journal of Chemical Kinetics 10, 503 (1978).
- W. C. Gardiner and R. D. Levine, "Thermochemical Properties of Atoms and Molecules in Specific Quantum States", ACS Symp. Ser. 56, 254 (1977); Journal of Chemical Physics 68, 4524 (1978).
- W. G. Mallard and W. C. Gardiner, Jr., "Absorption of the 3.39  $\mu\text{m}$  HeNe Laser Line by Methane from 300 to 2400 K", Journal of Quantitative Spectroscopy and Radiative Transfer, in press.
- D. B. Olson and W. C. Gardiner, Jr., "Combustion of Methane in Fuel-Rich Mixtures", Combustion and Flame 32, 151 (1978).
- W. C. Gardiner, D. B. Olson, and J. N. White, "Thermochemical Properties of HOCO and HOCO Formed from OH + CO", Chemical Physics Letters 53, 134 (1978).
- D. B. Olson, T. Tanzawa, and W. C. Gardiner, Jr., "Thermal Decomposition of Ethane," International Journal of Chemical Kinetics, in press.
- D. B. Olson and W. C. Gardiner, Jr., "Thermal Dissociation Rate of Ethane at the High Pressure Limit from 250 to 2500 K", Journal of Physical Chemistry, submitted.
- D. B. Olson, W. G. Mallard and W. C. Gardiner, Jr., "High-Temperature Absorption of the 3.39  $\mu\text{m}$  He-Ne Laser Line by Small Hydrocarbons", Applied Spectroscopy 32, 489 (1978).
- J. N. White and W. C. Gardiner, Jr., "Thermochemical Properties of the HSO Radical", Chemical Physics Letters, in press.

- J. N. White and W. C. Gardiner, Jr., "An Evaluation of Methane Combustion Mechanisms. II. Comparison of Model Predictions with Experimental Data from Shock-Initiated Combustion of  $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$ ," Journal of Physical Chemistry, in press.
- T. Tanzawa and W. C. Gardiner, Jr., "Thermal Decomposition of Acetylene," Seventeenth International Symposium on Combustion, Leeds, 1978 (The Combustion Institute, 1979), in press.
- T. Tanzawa and W. C. Gardiner, Jr., "Thermal Decomposition of Ethylene," International Journal of Chemical Kinetics, submitted.
- W. C. Gardiner, Jr., "Derivation of Elementary Reaction Rate Constants by Means of Computer Modeling," Journal of Physical Chemistry, in press.
- W. C. Gardiner, Jr., "Laser Absorption Methods for Characterizing High Temperature Gases," Characterization of High Temperature Vapors and Gases, NBS Symposium Proceedings, in press.

Appendix--Participating scientific personnel.

The following personnel participated in the research for all or part of the grant period. Degrees obtained at The University of Texas are noted by dates. Personnel with degrees from elsewhere are noted by their last university.

W. H. Brotherton  
W. C. Gardiner, Jr.  
J. H. Hardy (Ph.D. 1976)  
Y. Hidaka (Hiroshima University)  
T. Koike (Tohoku University)  
W. G. Mallard (Ph.D. 1975)  
D. B. Olson (Ph.D. 1977)  
M. H. Proffitt  
T. Tanzawa (Ph.D. 1978)  
J. N. White (B.S. 1978)